

7489

(12) UK Patent Application (19) GB (11) 2 104 091 A

(21) Application No **8217326**

(22) Date of filing **15 Jun 1982**

(30) Priority data

(31) **56/111693**

(32) **17 Jul 1981**

(33) Japan (JP)

(43) Application published  
**2 Mar 1983**

(51) INT CL<sup>3</sup>

**C11D 3/37**

(52) Domestic classification

**C5D 6B11C 6B12A**

**6B12B1 6B12F2 6B12G2A**

**6B12G2B 6B12K2 6B12L**

**U1S 1243 1245 1834 C5D**

(56) Documents cited

**None**

(58) Field of search

**C5D**

(71) Applicant

**Kao Soap Co. Ltd.,**

**(Japan),**

**14—10 Nihonbashi-**

**Kayabacho,**

**1-chome,**

**Chuo-ku,**

**Tokyo,**

**Japan**

(72) Inventors

**Takashi Ishii,**

**Tsutomu Nebashi,**

**Naoteru Ohtani,**

(74) Agents

**Withers and Rogers,**

**4, Dyer's Buildings,**

**Holborn,**

**London,**

**EC1N 2JT**

(54) **Detergent composition**

(57) A detergent composition comprises 0.01 to 10 percent by weight of an amphoteric copolymer obtained by co-polymerizing an anionic vinyl monomer having a

polymerizable unsaturated group with a cationic vinyl monomer having a polymerizable unsaturated group in a molar ratio of 1:99 to 99:1. The balance comprises optional additives and a carrier for the liquid or powder detergent composition.

GB 2 104 091 A

The chemical formulae appearing in the printed specification were submitted after the date of filing, the formulae originally submitted being incapable of being satisfactorily reproduced.

SPECIFICATION  
Detergent composition

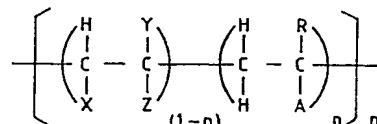
The present invention relates to a detergent composition containing a specific amphoteric polymer. More particularly, the present invention relates to a detergent composition having a deterging capacity remarkably improved by incorporating a specific amphoteric polymer obtained by copolymerizing a cationic vinyl monomer with an anionic vinyl monomer. 5

Polymers have been used as additives for detergents. For example, there have known detergent compositions containing polymers as a thickening agent stabilizer, protective colloid, builder, softener, encapsulating agent, hazing agent, pearlizing agent or skin- or hair-protecting agent. However, they have 10 been used merely according to the properties generally known as the characteristics of the high molecular compounds. 10

After investigations made for the purpose of finding a new application of polymers in detergent systems, the inventors have found that, surprisingly, a specific polymer greatly improves the detergency of a detergent composition particularly in the presence of a surfactant. The present 15 invention has been completed on the basis of this finding. 15

The present invention provides a detergent composition containing a specific amphoteric polymer obtained by copolymerizing a cationic vinyl monomer with an anionic vinyl monomer. In view of the deterging effects of the composition, it is noted that the effects of the amphoteric polymer in the present invention are utterly different from the known effects of high molecular surfactants not relating 20 directly to the detergency, such as a dispersing effect. 20

The amphoteric copolymer used in the present invention is obtained by copolymerizing an anionic vinyl monomer having a polymerizable unsaturated group with a cationic vinyl monomer having a polymerizable unsaturated group in a molar ratio of 1—99:99—1, preferably 20—80:80—20. The amphoteric copolymer thus obtained is represented by general formula (I):

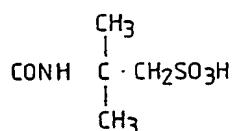


wherein:

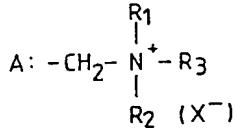
X: —H or —COOH  
Y: —H, —CH<sub>3</sub>, —CH<sub>2</sub>COOH or —OH

30

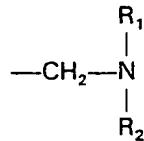
Z: —COOH, —SO<sub>3</sub>H, —CH<sub>2</sub>SO<sub>3</sub>H, —SO<sub>3</sub>H or



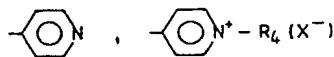
R: —H or —CH<sub>3</sub>



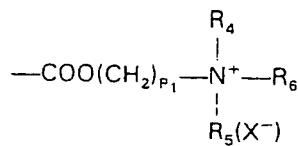
in which R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> each represent a C<sub>1</sub> to C<sub>3</sub> alkyl group and X<sup>−</sup> represents an anion such as a halogen or diethyl sulfate (the same shall apply hereinafter), 35



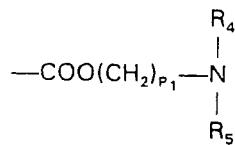
in which R<sub>1</sub> and R<sub>2</sub> each represent a C<sub>1</sub> to C<sub>3</sub> alkyl group,



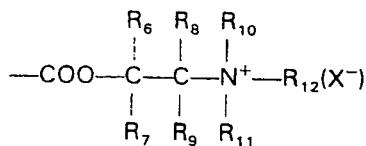
in which R<sub>4</sub> represents a C<sub>1</sub> to C<sub>3</sub> alkyl group,



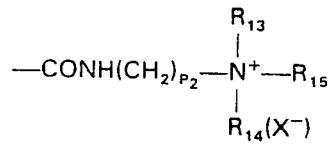
in which  $\text{R}_4$ ,  $\text{R}_5$  and  $\text{R}_6$  each represent a  $\text{C}_1$  to  $\text{C}_3$  alkyl group and  $\text{P}_1$  represents an integer of 2 to 4,



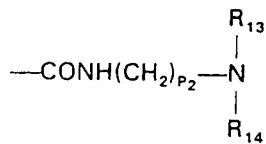
in which  $\text{R}_4$  and  $\text{R}_5$  each represent a  $\text{C}_1$  to  $\text{C}_3$  alkyl group and  $\text{P}_1$  represents an integer of 2 to 4,



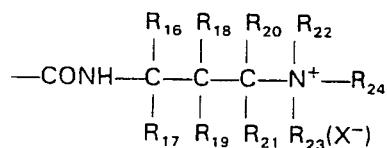
in which  $\text{R}_6$ ,  $\text{R}_7$ ,  $\text{R}_8$  and  $\text{R}_9$  each represent  $\text{H}$  or  $\text{CH}_3$  and  $\text{R}_{10}$ ,  $\text{R}_{11}$ , and  $\text{R}_{12}$  each represent a  $\text{C}_1$  to  $\text{C}_3$  alkyl group,



in which  $\text{R}_{13}$ ,  $\text{R}_{14}$  and  $\text{R}_{15}$  each represent a  $\text{C}_1$  to  $\text{C}_3$  alkyl group and  $\text{P}_2$  represents an integer of 2 to 4,



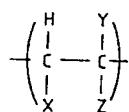
in which  $\text{R}_{13}$  and  $\text{R}_{14}$  each represent a  $\text{C}_1$  to  $\text{C}_3$  alkyl group and  $\text{P}_2$  represents an integer of 2 to 4, or



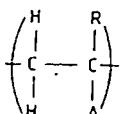
in which  $\text{R}_{16}$  to  $\text{R}_{21}$  each represents  $\text{H}$  or  $\text{CH}_3$  and  $\text{R}_{22}$  to  $\text{R}_{24}$  each represents a  $\text{C}_1$  to  $\text{C}_3$  alkyl group  $\rho$  represents a number of 0.01 to 0.99,  $\rho$  represents an integer of 5 to 10000, and  $\text{X}$ ,  $\text{Y}$  and  $\text{Z}$  may be an alkali metal salt, ammonium salt or alkanolamine salt.

15 The amphoteric polymer of the above general formula (I) according to the present invention is obtained by copolymerizing a cationic vinyl monomer with an anionic vinyl monomer. Those amphoteric polymers can be produced by a well known method. In the copolymerization, water is generally used as a solvent and potassium peroxodisulfate, potassium peroxodisulfate/sodium 20 hydrogensulfite or hydrogen peroxide/ $\text{Fe}^{2+}$  may be used as an initiator. The resulting copolymer may be used as such or after the purification. The purification is effected by dialysis or reprecipitation method.

The amphoteric copolymer of the present invention comprises anionic vinyl monomer structural units of the formula:



25 and cationic vinyl monomer structural units of the formula:



randomly arranged in a molar ratio of 1—99:99—1, preferably 20—80:80—20 to form a linear polymer having a molecular weight of 1,000 to 3,000,000. This amphoteric copolymer is produced by polymerizing a mixture of the above-mentioned anionic vinyl monomer and cationic vinyl monomer in a given ratio in the presence of a polymerization initiator in water generally under a nitrogen stream. The

5

5 polymerization is carried out generally at a temperature ranging from room temperature to 90°C for 2 to 24 h to obtain the intended copolymer having a molecular weight of preferably 3,000 to 1,000,000. Either solution polymerization or bulk polymerization method may be employed. The thus obtained copolymer may be reacted with an alkali metal hydroxide, ammonia or alkanolamine to form a salt.

5

The anionic monomer used may be any of anionic monomers having a polymerizable unsaturated 10 group and includes acrylic acid, methacrylic acid, itaconic acid, aconitic acid, hydroxyacrylic acid, maleic anhydride, fumaric acid, vinylsulfonic acid, allylsulfonic acid, methallylsulfonic acid, styrenesulfonic acid and 2-acrylamido-2-methylpropane-sulfonic acid.

10

The cationic monomer used may be any of cationic monomers having a polymerizable unsaturated group and includes 2-vinylpyridine, 4-vinylpyridine, dimethylaminoethyl methacrylate, 15 diethylaminoethyl methacrylate, dipropylaminoethyl methacrylate, dimethylaminopropylmethacrylamide, allyldimethylamine, allyldiethylamine, allyldipropylamine, methallyldimethylamine, methallyldiethylamine, methallyldipropylamine and methylated, ethylated or propylated derivative thereof.

15

The detergent composition of the present invention contains generally 0.01 to 10 wt.%, 20 preferably 0.05 to 5%, of the amphoteric polymer.

20

The detergent composition of the present invention contains 1 to 50 wt.% of a surfactant. An anionic, nonionic, cationic or amphoteric surfactant generally used in the art may be selected in the present invention suitably for the use. As the surfactant, there may be mentioned an anionic surfactant such as an alkyl sulfate, alkylbenzenesulfonate, alkylpolyoxyethylenesulfate,  $\alpha$ -olefinsulfonate, 25 alkanesulfonate, alkyl glyceryl ether sulfonate, alkyl or alkenylcarboxylate, alkenylsuccinate, N-acylsarcosinate, salt of carboxymethylated alkylpolyoxyethylene or alkylphosphate salt; a nonionic surfactant such as a fatty acid diethanolamide, dimethylalkylamine oxide, alkylpolyoxyethylene or alkylarylpolyoxyethylene; cationic surfactant such as an alkyltrimethylammonium salt, dialkyldimethylammonium salt or alkyl-(N-hydroxyethyl)-dimethylammonium salt; or an amphoteric 30 surfactant such as an alkylimidazole derivative, dimethylalkylbetaine or dimethylalkylsulfobetaine. The amphoteric polymer is used in an amount of 0.02 to 50 wt.%, preferably 0.25 to 25 wt.%, based on the surfactant according to the present invention. The amount of the surfactant may be determined suitably according to use of the detergent. In carrying out the present invention, the surfactant may be omitted in some cases.

30

35 The detergent composition of the present invention may contain also other components such as a solvent, e.g. a monoalcohol, dialcohol, glycerol, ethylene glycol monobutyl ether or diethylene glycol monomethyl ether, a hydrotrope, e.g. a benzenesulfonic acid salt, p-toluenesulfonic acid salt, m-xenesulfonic acid salt or urea, a chelating agent, an antiseptic, a dyestuff, a perfume, a U.V. absorber, an antioxidant, a hazing agent or thickening agent. The detergent composition of the present invention 40 is generally in the form of a liquid prepared by adding water to the detergent composition. Further, it may be in the form of a solid.

40

The detergent composition of the present invention can be used as a detergent for metals, machines, ships, textiles, glasswares, foods, tablewares, fibers and domestic appliances as well as a shampoo base. The properties required of such a detergent include deterging power, foam-increasing 45 property and rinsing properties (defoaming property, the touch, etc.). In the present invention, the larger the amount of the amphoteric polymer, the higher the capacities such as deterging power. However, an excessive amount of the amphoteric polymer might exert a harmful influence on physical properties of the product, such as stability and viscosity.

45

The following examples of synthesis of amphoteric polymers and the examples of the present 50 invention will further illustrate the invention, which by no means limit the invention.

50

### Synthesis Example 1

600 g of ion-exchanged water, 55 g of dimethylaminoethyl methacrylate, 30 g of methacrylic acid and 0.3 g of potassium peroxodisulfate were charged in a 1 l flask provided with a stirrer, thermometer, reflux condenser and nitrogen gas inlet. The polymerization reaction was carried out at 55 70°C under a nitrogen stream for 6 h. Then, the reaction mixture was cooled to room temperature and poured into 3000 g of acetone. An amphoteric polymer thus precipitated was filtered out. The weight of the polymer after drying under reduced pressure was 83 g. The rate of polymerization was 98%.

55

### Synthesis Example 2

An anionic monomer and a cationic monomer as shown in Table 1 were copolymerized in a molar 60 ratio of 1:1 in the same manner as in the above Synthesis Example 1. The synthesis conditions were as follows:

60

5  
Ion exchanged water 600 ml  
Monomers 0.5 M  
Temperature 70°C  
Reaction time 6 h  
Initiator  $K_2S_2O_8$

5

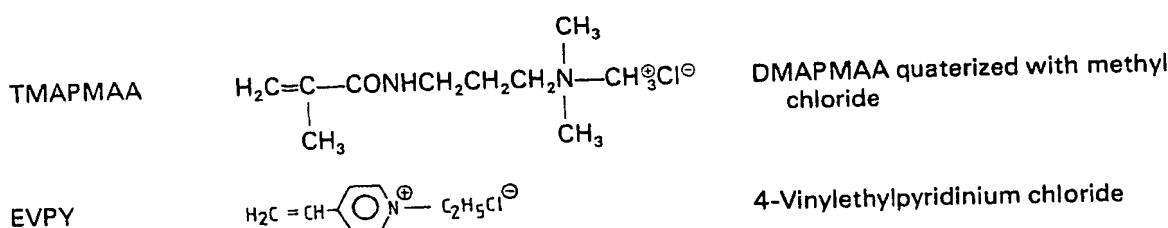
Table 1  
Synthesis No. Anionic monomer Cationic monomer

10	1	AA	DMAEMA	
	2	AA	TMAEMA	
	3	AA	EDMAEMA	10
	4	MA	TMAEMA	
	5	MA	EDMAEMA	
	6	SS	TMAEMA	
	7	SS	TMAPMAA	
15	8	AAMPS	EDMAEMA	15
	9	AAMPS	EVPY	
	10	AAMPS	TMAPMAA	
	11	ALS	EDMAEMA	
	12	VS	EDMAEMA	
20	13	VS	DMAPMAA	20

wherein:

AA	$H_2C=C$ H —COOH	Acrylic acid	
MA	$H_2C=C$ —COOH   CH <sub>3</sub>	Methacrylic acid	
SS	$H_2C=CH$ —(C <sub>6</sub> H <sub>4</sub> )—SO <sub>3</sub> H	Styrenesulfonic acid-(4)	
25 AAMPS	$H_2C=CH$ —CONH C—CH <sub>2</sub> SO <sub>3</sub> H   CH <sub>3</sub>	2-Acrylamido-2-methylpropanesulfonic acid	25
ALS	$H_2C=CH$ —CH <sub>2</sub> SO <sub>3</sub> H	Allylsulfonic acid	
VS	$H_2C=CH$ —SO <sub>3</sub> H	Vinylsulfonic acid	
DMAEMA	$H_2C=C$   CH <sub>3</sub> —COOCH <sub>2</sub> CH <sub>2</sub> N   CH <sub>3</sub>   CH <sub>3</sub>	Dimethylaminoethylmethacrylate	
DMAPMAA	$H_2C=C$   CH <sub>3</sub> —CONHCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> N   CH <sub>3</sub>   CH <sub>3</sub>	Dimethylaminopropylmethacrylamide	
30 TMAEMA	$H_2C=C$   CH <sub>3</sub> —COOCH CH N—CH <sup>2</sup> Cl <sup>2</sup>   CH <sub>3</sub>	DMAEMA quaterized with methyl chloride	30
EDMAEMA	$H_2C=C$   CH <sub>3</sub> —COOCH <sub>2</sub> CH <sub>2</sub> N—C <sub>2</sub> H <sub>5</sub> C <sub>2</sub> H <sub>5</sub> SO <sub>4</sub>   CH <sub>4</sub>	DMAEMA quaterized with diethyl sulfate	

5



In the following examples wherein detergent compositions containing polymers of Synthesis Nos. 1 to 13 shown in Table 1 were tested, the properties of the detergents were examined according to the following methods:

### a) Detergency

10 a) Detergency  
0.1% of Sudan III (a red dyestuff) used as an indicator was added to beef tallow. 5 g of the mixture was applied to each porcelain dish (diameter: 25 cm) and rubbed with a sponge impregnated with 10 g of a detergent and 20 g of water. Detergency of the detergent is represented by the number of dishes cleaned with the sponge until the beef tallow could no more be removed completely.

### b) Foaming power

15 b) **foaming power**  
A foaming power of 0.5% detergent solution containing 0.1% of a commercially available butter as a dirt was measured. 40 cc of the butter-containing detergent solution was charged in a glass cylinder having a diameter of 5 cm and the solution was stirred by means of a rotary stirrer for 10 min. Immediately thereafter, the height of the foam was measured.

### c) Water repellency

c) **Water repellency** A commercially available 200 ml glass was washed well with a cleanser. After confirming that the glass could not repel water any more, the glass was rinsed with ion-exchanged water and dried. 20 150 ml of 1% aqueous detergent solution was charged in the glass, stirred by means of a rotary stirrer for 30 min and poured out. 200 ml of city water was charged in the glass, left to stand for 30 sec, and then poured out. This procedure was repeated three times. Water repellency after the pouring of water for the fourth time and the state of the glass after left to stand for one day were observed.

d) Rinse

25 d) **Rinse** 100 cc of 0.25% aqueous detergent solution (temp.: 20°C) was placed in a 500 cc separatory funnel and shaken given times. Then, the solution was poured out and the amount of the foam was measured. Thereafter, 50 cc of rinsing water (20°C) was poured thereinto and the separatory funnel was rotated slowly 10 times. This procedure was repeated until the foam disappeared to determine the number of times of rinse.

### 30 Example 1

A liquid detergent of the following composition was prepared:

Sodium straight-chain alkylbenzenesulfonate	20 wt. %
Coconut fatty acid diethanolamide	5 wt. %
Polymer	1 wt. %
Water	balance

35 Water  
 Detergency and foaming power of the detergent were measured to obtain the results shown in  
 Table 2.

**Table 2**  
*Number of dishes*

	<i>Polymer</i>	<i>cleaned</i>	<i>(mm/m)</i>
40	Not used	2	55
	Synthesis No. 1	4—5	75
	Synthesis No. 3	7—8	80
	Synthesis No. 4	7	95
	Synthesis No. 6	6	85
	Synthesis No. 8	5—6	80
	Synthesis No. 10	5	85
	Synthesis No. 12	7—8	90
45			

It is understood from Table 2 that the detergency and foaming power were remarkably improved by the incorporation of the polymer.

**Example 2**

A liquid detergent of the following composition was prepared:

	$  \begin{array}{c}  \text{CH}_3 \\    \\  \text{C}_{12}\text{H}_{25}-\text{N}-\text{CH}_3^{\oplus}\text{Cl}^{\ominus} \\    \\  \text{CH}_3  \end{array}  $	5 wt. %
5	Polymer	0.5 wt. %
	Ethanol	2 wt. %
	Water	balance
		5

Water repellency of the detergent was examined to obtain the results shown in Table 3.

**Table 3**

*Polymer*      *Water repellency*

10	Not used	observed	10
	Synthesis No. 2	not observed	
	Synthesis No. 3	not observed	
	Synthesis No. 5	not observed	

**Example 3****[Test of preference for foams]**

Preference for foams were examined by a panel comprising 30 female testers. In the test, the preference for foams was examined by a pair comparison method using detergent compositions A and B in the same manner as in the deterging power test. The compositions tested are shown in Table 4 and the test results are shown in Table 5.

**20 Criteria**

- +2: A was preferred.
- +1: A was relatively preferred.
- 0: Preferences for A and B were equal.
- 1: B was relatively preferred.
- 2: B was preferred.

20

15

25

25

**Table 4**

	<i>Components</i>	<i>Composition No.</i>			<i>Comparative Example 4</i>
		1	2	3	
30	Sodium alkyl ether sulfate*	20	20	20	20
	Coconut fatty acid diethanolamide	5	5	5	5
	Ethanol	5	5	5	5
	Polymer				
	Synthesis No. 3	0.3			
35	Synthesis No. 11		0.3		
	Synthesis No. 13			0.3	
	Water	balance	balance	balance	balance

**Table 5**

40	<i>Combination (A and B)</i>	<i>Marks</i>					<i>Judgement</i>
		+2	+1	0	-1	-2	
	Compositions Nos. 1 vs. 4	9	12	7	2	0	No. 1 was preferred to No. 4 (+28)
45	Composition Nos. 2 vs. 4	4	7	16	3	0	No. 2 was preferred to No. 4 (+12)
	Composition Nos. 3 vs. 4	7	9	10	4	1	No. 3 was preferred to No. 4 (+17)

(Note)\* Average carbon chain length: 12, ethylene oxide (3 mol) adduct.

**Example 4**

Rinsing tests of the compositions of the present invention and polymer-free comparative compositions were carried out. The compositions are shown in Table 6 and the test results are shown in Table 7.

50

Table 6

Table 7

	<i>Composition No.</i>	<i>Amount of foam (ml)</i>	<i>Number of times of rinse</i>	
5	5	350	3	5
	6	350	3—4	
	7	400	3—4	
	8	350	3	
10	9	300	3	10
	10	350	4	
	11	350	4	
	12	350	3—4	
	13	400	5—6	
	14	400	6	

**Claims**

15 1. A detergent composition which comprises 0.01 to 10 percent by weight of an amphoteric copolymer obtained by co-polymerizing an anionic vinyl monomer having a polymerizable unsaturated group with a cationic vinyl monomer having a polymerizable unsaturated group in a molar ratio of 1:99 to 99:1, the balance being optional additives and a carrier for the liquid or powder detergent composition. 15

20 2. A detergent composition as claimed in Claim 1, which further comprises from 1 percent by weight to 50 percent by weight of a surfactant. 20

3. A detergent composition as claimed in Claim 2, where said amphoteric copolymer is contained in an amount of 0.02 to 50 percent by weight, based on the surfactant.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1983. Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained

